

# The Shear Viscosity and Mutual Diffusion Coefficients of Binary Mixtures Using the Modified Enskog Theory<sup>1</sup>

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We use an extended form of the modified Enskog Theory (MET) to calculate viscosity and mutual diffusion coefficients for several binary mixtures. Second and third virial coefficients are required for the calculations. We find that the extended MET provides predictions of the shear viscosity for He–Ar and Ne–Ar mixtures with an accuracy of 2% at densities up to  $6 \text{ mol} \cdot \text{L}^{-1}$ . Extended MET values of mutual diffusion coefficients of binary mixtures in which the mole fraction of one component approaches zero were calculated for He–Ar and Kr–Ar mixtures. The MET values fall within 10–15% of the experimental data at densities up to  $11 \text{ mol} \cdot \text{L}^{-1}$ .

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**KEY WORDS:** argon; diffusion; Enskog theory; helium; krypton; mixtures; modified Enskog theory; neon; virial coefficients; viscosity.

## 1. INTRODUCTION

Recently [1] we proposed a method for extending the modified Enskog theory (MET) to multicomponent mixtures and showed that the extended MET successfully predicted the shear viscosities for Ne–Ar and He–Ar mixtures at moderate densities. For Ne–Ar mixtures the extended MET predictions fell within 2% of the experimental data at densities up to  $6 \text{ mol} \cdot \text{L}^{-1}$ . For He–Ar the predictions were also within 2% of the experimental results, limited to densities of about  $2 \text{ mol} \cdot \text{L}^{-1}$  by the experimental data.

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In this paper we continue testing the extended MET by comparing calculations of the shear viscosity and mutual diffusion coefficients to experimental measurements. The extended MET [1] uses the revised Enskog theory expressions for the transport coefficients [2]. Those expressions depend on the temperature,  $T$ , the number density,  $n$ , the hard-sphere diameters,  $\{\sigma_{ij}\}$ , the masses,  $\{m_i\}$ , and the hard-sphere radial distribution functions at contact,  $\{\chi_{ij}\}$ . (Here  $i$  and  $j$  are species labels.) The transport coefficients of a real system are approximated by using the Enskog theory expressions with  $\{\sigma_{ij}\}$  and  $\{\chi_{ij}\}$  replaced by expressions that depend on the virial coefficients of the real system.

(a) The  $\sigma_{ij}$  are determined by setting

$$B_{ij}^{\text{hs}} (= 2\pi N_A \sigma_{ij}^3/3) = B_{ij}^r + T \frac{dB_{ij}^r}{dT} \quad (1)$$

where  $B_{ij}$  is a second virial coefficient,  $N_A$  is the Avogadro number, and a superscript  $r$  denotes real fluid properties. Thus  $\sigma_{ij}$  becomes temperature dependent.

(b) The  $\chi_{ij}$  are determined by setting

$$B_{ij}^{\text{hs}} \chi_{ij} = B_{ij}^r + T dB_{ij}^r/dT + \sum_k (C_{ijk}^r + T dC_{ijk}^r/dT) n_k + \dots \quad (2)$$

where  $C_{ijk}^r$  is the real fluid third virial coefficient and the right-hand side includes additional terms involving higher-order virial coefficients.

Using the MET to predict transport properties of mixtures is in theory easy, requiring only the virial coefficients and their derivatives with respect to temperature. In practice these values are difficult to find. The bulk of this work consisted in exploring methods for determining the virial coefficients, and we limit our study to densities low enough so that only virial coefficients through the third are required.

## 2. VISCOSITY CALCULATIONS

In this section we report our extended MET calculations of shear viscosity for Ne–Ar and He–Ar mixtures. The expression for the Enskog theory shear viscosity was obtained from Ref. 2; the third Enskog approximation was used.

### 2.1. Neon–Argon

We used two methods to determine the virial coefficients of Ne–Ar mixtures. In the first method, we used the equations of state of Gosman et

al. [3], Michels et al. [4], and Kestin et al. [5] to determine  $B_{11}(T)$ ,  $B_{12}(T)$ ,  $B_{22}(T)$ ,  $C_{111}(T)$ , and  $C_{222}(T)$ . We used the mixing rule suggested by Brewer and Vaughn [6] to determine  $C_{112}$  and  $C_{122}$ :

$$C_{112} = [C_{111}^2(T) C_{222}(T)]^{1/3} \quad (3)$$

and

$$C_{122} = [C_{111}(T) C_{222}^2(T)]^{1/3} \quad (4)$$

(See Ref. 1 for details.)

For the second method we used the experimental data of Kestin et al. [5] to determine the constants  $\sigma_{ij}$  and  $\varepsilon_{ij}/k_B$  for a Lennard-Jones 6-12 potential and computed  $B_{ij}(T)$  and  $C_{ijk}(T)$  using adaptive numerical integration, where  $k_B$  is the Boltzmann constant. Since both the virial coefficients and their temperature derivatives are used in the extended MET, we chose  $\sigma_{ij}$  and  $\varepsilon_{ij}/k_B$  such that  $B_{ij}^{LJ}(T) = B_{ij}^r(T)$  and  $dB_{ij}^{LJ}(T)/dT = dB_{ij}^r(T)/dT$ , where the superscript LJ labels second virial coefficients computed using a Lennard-Jones potential. By introducing the reduced temperature  $T^* = k_B T/\varepsilon_{ij}$  and a reduced distance  $r^* = r/\sigma_{ij}$ , where  $r$  is the argument of the L-J potential, it is easy to see that  $B_{ij}^*/(T^* dB_{ij}^*/dT^*)$

**Table I.** Second and Third Virial Coefficients for Ne-Ar Mixtures at  $T = 298.15$  K

	Method 1 <sup>a</sup>	Method 2 <sup>b</sup>	Method 3 <sup>c</sup>
$B_{11}$	$1.0 \times 10^{-2}$	$1.0 \times 10^{-2}$	$1.16 \times 10^{-2}$ [ $L \cdot \text{mol}^{-1}$ ]
$dB_{11}/dT$	$5.68 \times 10^{-2}$	$5.68 \times 10^{-2}$	$2.07 \times 10^{-2}$ [ $L \cdot \text{mol}^{-1} \cdot K^{-1}$ ]
$B_{12}$	$1.08 \times 10^{-2}$	$1.08 \times 10^{-2}$	
$dB_{12}/dT$	$5.0 \times 10^{-5}$	$5.0 \times 10^{-5}$	
$B_{22}$	$-1.54 \times 10^{-2}$	$-1.54 \times 10^{-2}$	
$dB_{22}/dT$	$2.0 \times 10^{-4}$	$2.0 \times 10^{-4}$	
$C_{111}$	$5.05 \times 10^{-4}$	$4.30 \times 10^{-4}$	$2.5 \times 10^{-4}$ [ $L^2 \cdot \text{mol}^{-2}$ ]
$dC_{111}/dT$	$2.32 \times 10^{-8}$	$-1.91 \times 10^{-7}$	$-2.4 \times 10^{-8}$ [ $L^2 \cdot \text{mol}^{-2} \cdot K^{-1}$ ]
$C_{112}$	$6.19 \times 10^{-4}$	$4.2 \times 10^{-4}$	
$dC_{112}/dT$	$-4.09 \times 10^{-7}$	$-1.97 \times 10^{-7}$	
$C_{122}$	$7.58 \times 10^{-4}$	$6.1 \times 10^{-4}$	
$dC_{122}/dT$	$-1.04 \times 10^{-6}$	$-5.32 \times 10^{-7}$	
$C_{222}$	$9.3 \times 10^{-4}$	$9.35 \times 10^{-4}$	
$dC_{222}/dT$	$-1.9 \times 10^{-6}$	$-1.6 \times 10^{-6}$	

<sup>a</sup> Values extracted from Refs. 3-5.

<sup>b</sup> Values obtained using L-J parameters given in Table IV.

<sup>c</sup> Values obtained using L-J parameters given in Ref. 7.

is independent of  $\sigma_{ij}$ . Here  $B_{ij} = 2\pi N_A \sigma_{ij}^3 B_{ij}^*/3$ . We determined  $\varepsilon_{ij}/k_B$  by finding that  $T^*$  such that  $B_{ij}^*/(T^* dB_{ij}^*/dT^*) = B_{ij}^r/(T dB_{ij}^r/dT^r)$ . Then  $\varepsilon_{ij}/k_B = T/T^*$  and  $\sigma_{ij} = [3B_{ij}/(2\pi N_A B_{ij}^*)]^{1/3}$ .

For Ar (species 2) we found  $\sigma_{22} = 3.4157 \text{ \AA}$  and  $\varepsilon_{22}/k_B = 118.1 \text{ K}$ ; for Ne (species 1) we found  $\sigma_{11} = 3.08 \text{ \AA}$  and  $\varepsilon_{11}/k_B = 56.4 \text{ K}$ ; for the cross terms we found  $\sigma_{12} = 3.056 \text{ \AA}$  and  $\varepsilon_{12}/k_B = 52.6 \text{ K}$ . We note that the value of  $\varepsilon_{11}/k_B$  for Ne was considerably higher than that found in the literature; for instance, Hirschfelder et al. [7] give values around 35 K. It was necessary to bring  $\varepsilon_{11}/k_B$  to these high values in order to achieve the proper value of  $dB_{11}/dT$ . Typically, when the literature values for the force constants were used, the second virial coefficient would be close to the experimental values, but the temperature derivative of the second virial coefficient would deviate considerably from the experimental values. (See Table I.)

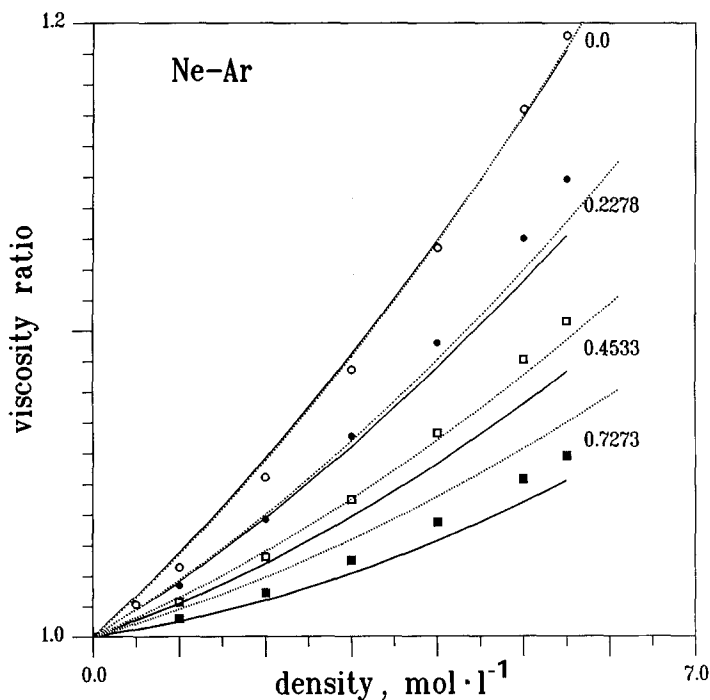


Fig. 1. The Ne-Ar shear viscosity ratio,  $\eta/\eta_0$ , versus density at  $T = 298.15 \text{ K}$  for Ne mole fractions of 0, 0.2278, 0.4533, and 0.7273. The circles and squares represent the data of Ref. 5; the extended MET predictions are given by the solid and dotted curves. Experimental values for the virial coefficients were used to obtain the solid curves; virial coefficients calculated using a L-J potential were used to obtain the dotted curves.

Once  $\epsilon_{ij}/k_B$  and  $\sigma_{ij}$  were determined,  $C_{ijk}$  and  $dC_{ijk}/dT$  were obtained numerically. In Table I we have listed the results of the calculations, as well as those obtained from the experimental data (method 1). Figure 1 shows  $\eta/\eta_0$  as a function of density for several values of the Ne mole fraction, where  $\eta$  is the shear viscosity and  $\eta_0$  is the shear viscosity of the mixture in the dilute gas limit. Both methods yield values for  $\eta/\eta_0$  that agree with experimental values [5] to within 2% for densities up to 6 mol per liter, except for the case of pure Ne. For pure Ne, method 2 led to values of  $\eta/\eta_0$  that were as much as 4% higher than the measured values. The somewhat larger deviations of method 2 result from the experimental data are due to the poor approximation to  $dC_{111}/dT$  using a L-J potential.

## 2.2. He-Ar

In Table II we list the virial coefficients and their temperature derivatives. The L-J parameters are given in Table IV. In this case the differences between method 1 and method 2 are small and thus both methods lead to MET predictions of  $\eta/\eta_0$  that are quite similar. In Fig. 2 we compare the MET predictions to the data of Iwasaki and Kestin [8]. As in the Ne-Ar case, the predicted results lie within 2% of the experimental data and are least accurate for pure He.

Table II. Second and Third Virial Coefficients for He-Ar Mixtures at 293.15 K

	Method 1 <sup>a</sup>	Method 2 <sup>b</sup>
$B_{11}$	$1.19 \times 10^{-2}$	$1.19 \times 10^{-2}$ [L · mol <sup>-1</sup> ]
$dB_{11}/dT$	$-3.09 \times 10^{-6}$	$-3.10 \times 10^{-2}$ [L · mol <sup>-1</sup> · K <sup>-1</sup> ]
$B_{12}$	$1.79 \times 10^{-2}$	$1.79 \times 10^{-2}$
$dB_{12}/dT$	$1.78 \times 10^{-5}$	$1.81 \times 10^{-5}$
$B_{22}$	$-1.62 \times 10^{-2}$	$-1.62 \times 10^{-2}$
$dB_{22}/dT$	$2.10 \times 10^{-4}$	$2.10 \times 10^{-4}$
$C_{111}$	$1.09 \times 10^{-4}$	$1.05 \times 10^{-4}$ [L <sup>2</sup> · mol <sup>-2</sup> ]
$dC_{111}/dT$	$-2.13 \times 10^{-7}$	$-1.21 \times 10^{-7}$ [L <sup>2</sup> · mol <sup>-2</sup> · K <sup>-1</sup> ]
$C_{112}$	$2.08 \times 10^{-4}$	$1.45 \times 10^{-4}$
$dC_{112}/dT$	$-9.09 \times 10^{-7}$	$-1.49 \times 10^{-7}$
$C_{122}$	$6.48 \times 10^{-4}$	$5.64 \times 10^{-4}$
$dC_{122}/dT$	$-1.04 \times 10^{-6}$	$-5.32 \times 10^{-7}$
$C_{222}$	$9.69 \times 10^{-4}$	$9.66 \times 10^{-4}$
$dC_{222}/dT$	$-1.74 \times 10^{-6}$	$-1.71 \times 10^{-6}$

<sup>a</sup> Values extracted from Refs. 3-5.

<sup>b</sup> Values obtained using L-J parameters given in Table IV.

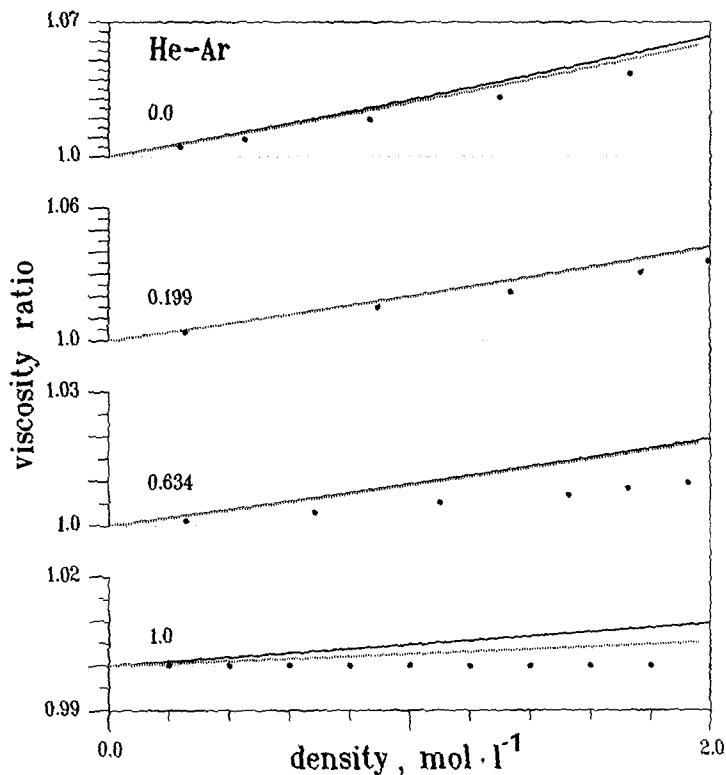


Fig. 2. The He-Ar shear viscosity ratio,  $\eta/\eta_0$ , versus density at  $T = 293.15$  K for He mole fractions of 0, 0.199, 0.634, and 1.0. The circles represent the data of Ref. [8]; the extended MET predictions are given by the solid and dotted curves. Experimental values for the virial coefficients were used to obtain the solid curves; virial coefficients calculated using a L-J potential were used to obtain the dotted curves.

### 3. MUTUAL DIFFUSION CONSTANTS

In this section we compare the extended MET predictions of the mutual diffusion coefficient,  $D$ , with experimental data for two mixtures: He-Ar and Ar-Kr. In both mixtures only the case where the mole fraction of one component approaches zero is examined. In this limiting case the revised Enskog theory diffusion constant [2] is relatively easy to evaluate. We find that

$$\rho D / (\rho D)_0 = 1/\chi_{12} \quad (5)$$

**Table III.** Second and Third L-J Virial Coefficients for He-Ar at 298.15 K

$B_{11}$	$1.1887 \times 10^{-2}$ [L · mol <sup>-1</sup> ]	$dB_{11}/dT$	$-3.1317 \times 10^{-6}$
$B_{12}$	$1.8011 \times 10^{-2}$	$dB_{12}/dT$	$1.7249 \times 10^{-5}$
$B_{22}$	$-1.5118 \times 10^{-2}$	$dB_{22}/dT$	$2.023 \times 10^{-4}$
$C_{111}$	$1.0472 \times 10^{-4}$ [L <sup>2</sup> · mol <sup>-2</sup> ]	$dC_{111}/dT$	$-1.1846 \times 10^{-7}$
$C_{112}$	$1.819 \times 10^{-4}$	$dC_{112}/dT$	$-2.2625 \times 10^{-8}$
$C_{122}$	$5.617 \times 10^{-4}$	$dC_{122}/dT$	$-6.09 \times 10^{-7}$
$C_{222}$	$9.5776 \times 10^{-4}$	$dC_{222}/dT$	$-1.6137 \times 10^{-6}$

where  $\rho$  is the mass density and  $(\rho D)_0$  is the limit of  $\rho D$  as  $\rho \rightarrow 0$ . Thus, the extended MET expression for  $D$ , denoted  $D^{\text{MET}}$ , is

$$D^{\text{MET}} = \frac{(\rho D)_0}{\rho} \left/ \left[ 1 + \frac{(C_{112} + TdC_{112}/dT)n}{B_{12} + TdB_{12}/dT} + \dots \right] \right. \quad (6)$$

where  $n$  is the number density and species 2 is the trace component.

### 3.1. He-Ar

Virial coefficients were determined by the procedure detailed in Section 2.1 by determining the L-J parameters  $\sigma_{ij}$  and  $\epsilon_{ij}/k_B$  from the experimental data, then using the adaptive integration program to determine the virial coefficients. Table III lists the virial coefficients used. These values and Eq. (6) were then used to find the diffusion coefficient.

Diffusion coefficients were calculated for He-Ar mixtures with trace quantities of Ar and trace quantities of He. The results were compared with the data of Balenovic et al. [9], who report diffusion coefficients at  $T = 298.15$  K and pressures beginning at 272 atm. This pressure is somewhat

**Table IV.** Lennard-Jones (6-12) Potential Parameters

	$\sigma$ (Å)	$\epsilon/k_B$ (K)
He	2.6306	7.294
Ne	3.086	56.4
Ar	3.4157	118.1
Kr	2.259	360
He-Ar	3.094	26.03
Ne-Ar	3.056	52.6
Kr-Ar	3.741	131

beyond the limits of the modified Enskog theory when only second and third virial coefficients are used. We find an error of about 5% for compressibility calculations at this pressure using only the second and third virial coefficients.

For He-Ar mixtures at 272 atm and  $T = 298.15$  K with trace amounts of helium, Balenovic et al. find  $D = 1.95 \times 10^{-3} \pm 0.04 \text{ cm}^2 \cdot \text{s}^{-1}$ ; Eq. (6) yields a value of  $2.198 \times 10^{-3}$ , about 10% higher. For trace amounts of Ar under the same conditions, the experimental value is  $2.80 \times 10^{-3} \pm 0.06 \text{ cm}^2 \cdot \text{s}^{-1}$ , and the MET prediction is  $2.75 \times 10^{-3} \text{ cm}^2 \cdot \text{s}^{-1}$ .

### 3.2. Ar-Kr

For this mixture Kr (species 2) is the trace component. The virial coefficient data of Schramm et al. [10] were used to find force constants  $\sigma_{12}$  and  $\varepsilon_{12}/k_B$  as described earlier. Force constants for pure Kr were determined by fitting the experimental data of Beattie et al. [11]. For pure argon, the force constants determined earlier were used. (See Table IV.)

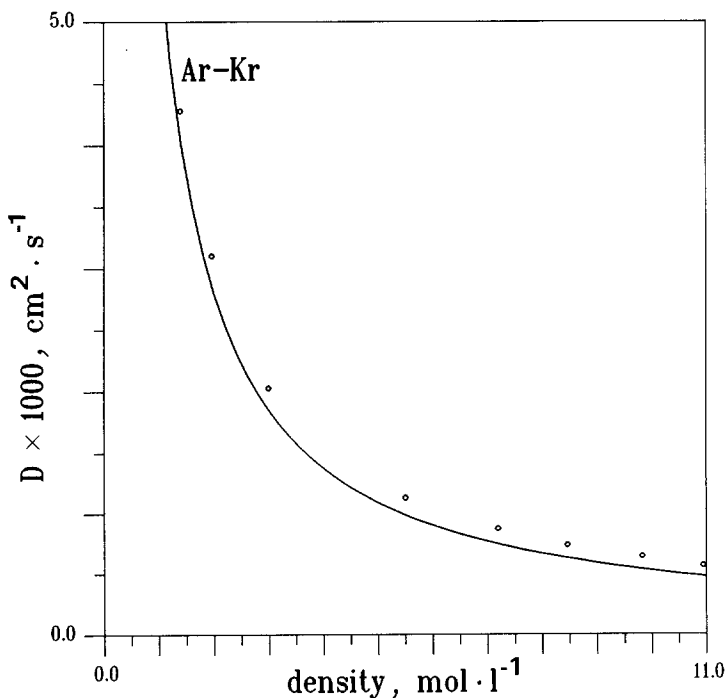


Fig. 3. The Ar-Kr mutual diffusion constant for trace amounts of Kr at  $T = 308.15$  K. The experimental data of Ref. 12 are represented by the circles; the extended MET prediction is represented by the solid curve.



These force constants were used to calculate second and third virial coefficients and their derivatives, which were then applied to the MET to calculate  $D$  at  $T=308.15$  K. In Fig. 3 we plot the experimental results of Durbin and Kobayashi [12] and compare them with extended MET values. At a density of 11 mol/L the extended MET prediction is about 15% too small. If one plots  $F=\rho D/(\rho D)_0$  versus  $\rho$  it becomes apparent that even at very low densities the slope of  $F^{\text{MET}}(\rho)$  has the wrong sign. The slope  $F^{\text{MET}}(\rho)$  can be adjusted, as suggested by Durbin and Kobayashi [12], by changing  $\varepsilon_{12}/k_B$ . It seems more likely that the Enskog value of the diffusion coefficient is lower than the true hard-sphere coefficient [13].

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